

The University of Chicago

THE ADDITION OF BISULFITE TO
UNSATURATED SUBSTANCES

A DISSERTATION SUBMITTED TO THE FACULTY
OF THE DIVISION OF THE PHYSICAL SCIENCES
IN CANDIDACY FOR THE DEGREE OF DOCTOR
OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY
AUGUST, 1940

By
REMSEN TEN EYCK SCHENCK

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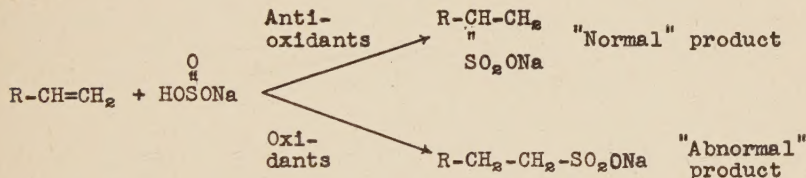
The author wishes to acknowledge his twofold indebtedness in the production of this work to Professor M. S. Kharasch for unfailing inspiration and to Doctor F. R. Mayo for constructive criticism.



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INTRODUCTION

Although it has been known for over half a century that bisulfites will add to most olefins to produce sulfonic acids, it was not established until 1938, by Kharasch, May, and Mayo,¹ that oxidizing agents are indispensable to the reaction, and that no interaction involving a simple double bond can occur in the absence of oxidants or the presence of antioxidants. In an investigation embracing ethylene, propylene, isobutylene, allyl alcohol, cinnamyl alcohol, and styrene, these workers demonstrated that the entering sulfonic acid group becomes attached to the terminal carbon atom (in the case of cinnamyl alcohol, to that more remote from the phenyl nucleus), giving rise to the "abnormal" product, in terms of Markownikoff's rule (cf. the second of the alternative routes below). The "normal" reaction in this addition apparently does not take place:



These authors further noted that styrene exhibited several unique characteristics. The reactions of this compound with bisulfite have since been more exhaustively investigated and the results incorporated in Part II of this work. Part I is concerned with a study of the addition of bisulfite to the internal double bonds in such olefins as pentene-2, trimethylethylene, and cyclohexene. This class was selected in the hope that this reaction, since only one of the two theoretically possible products had heretofore been obtainable, would help clarify the problem

¹Kharasch, May, and Mayo, J. Org. Chem., **3**, 174 (1938). A comprehensive review of the earlier literature is included in this article.

of "abnormal" addition of HBr to similar bonds, only three instances of which have so far been reported.² The results fell short of expectations in this regard but proved of value in themselves, since for the first time evidence of the formation of two isomeric sulfonic acids by this reaction has been found.

²Walling, Kharasch, and Mayo, J. Am. Chem. Soc., **61**, 1711, 2693 (1939).

PART I

THE ADDITION OF BISULFITE TO INTERNAL DOUBLE BONDS

DISCUSSION

The characteristics of the bisulfite reaction have been found to depend, in general, on seven major variables, namely: the nature of the oxidant, its concentration, the solvent, the nature of the olefin, its concentration, the temperature, and the pH or sulfite-bisulfite balance of the solution. The effect of temperature has not been studied beyond the observation that its influence on the rate of reaction is positive. The concentration of any liquid olefin, moreover, is constant in a biphasic reaction if sufficiently hard shaking is employed, while the range of pressures and consequent solubilities over which the gaseous members of the series may conveniently be studied is too short to afford many data. The remaining five factors, however, were investigated in some detail.

Three oxidants are known which react with bisulfite sufficiently slowly to permit addition to take place: perdisulfate and nitrite ions and molecular oxygen. The latter two were tested in this inquiry. In the case of highly reactive olefins, such as trimethylethylene and pentene-2, oxygen at low pressures is slightly more efficient than nitrite, even when the latter is introduced very slowly. This order is reversed for less active double bonds, e.g. that present in 2,4,4-trimethylpentene-2. The data on chain lengths and comparative yields are presented in Table 1. It should be noted that substitution occurs only in the presence of oxygen.

Since the chain initiators are also the chain breakers, the addition reaction will be favored by low concentrations of oxidizing agents. Higher concentrations increase the proportion of unsaturated products while reducing the overall yield.

The mutual solvents tested in an attempt to increase the miscibility of the two phases, methyl, ethyl, and tertiary butyl alcohols and dioxane, were without effect on the interaction of the more reactive olefins with bisulfite up to the limit of miscibility with molar bisulfite solutions, some 10 volume per cent of organic solvent in the salt solution. Inert organic diluents insoluble in water, such as ligroin, did not diminish

TABLE 1

THE ADDITION OF BISULFITE TO INTERNAL DOUBLE BONDS^a

Olefin	Oxygen Tension, mm of Hg	pH		Per Cent Total Yield on Sulfites Reacted	Per Cent Substi- tution in Product	Remarks
		Initial	Final			
Cyclohexene...	760	6.3	2.0	15	4 ^b	NaHSO ₃ - Na ₂ SO ₃
Cyclohexene...	760	6.5	7.5	35	4 ^b	NaHSO ₃ - Na ₂ SO ₃
Cyclohexene...	760	6.7	10+	24	3 ^b	NaHSO ₃ - Na ₂ SO ₃
Cyclohexene...	760	5.92	1-	20	16	NH ₄ HSO ₃ - (NH ₄) ₂ SO ₃
Cyclohexene...	152	5.92	2.69	64	0	NH ₄ HSO ₃ - (NH ₄) ₂ SO ₃
Cyclohexene...	30	5.92	8.39	93	0	NH ₄ HSO ₃ - (NH ₄) ₂ SO ₃
Cyclohexene...	c	4.91	6.3	55	2 ^d	NaHSO ₃
Cyclohexene...	e	4.90	6.8	84	0	NaHSO ₃
Pentene-2.....	760	5.92	7.07	80	1.5	NH ₄ HSO ₃ - (NH ₄) ₂ SO ₃
Pentene-2.....	152	5.92	8.55	90	0	NH ₄ HSO ₃ - (NH ₄) ₂ SO ₃
Pentene-2.....	30	5.64	7.89	96	0	NH ₄ HSO ₃ - (NH ₄) ₂ SO ₃
Pentene-2.....	f	4.91	6.84	80	0	NaHSO ₃
Trimethyl ethylene....	760	5.92	8.75	90	5	NH ₄ HSO ₃ - (NH ₄) ₂ SO ₃
Trimethyl ethylene....	152	5.64	8.34	93	0	NH ₄ HSO ₃ - (NH ₄) ₂ SO ₃
Trimethyl ethylene....	30	5.64	8.41	98+	0	NH ₄ HSO ₃ - (NH ₄) ₂ SO ₃
Trimethyl ethylene....	g	5.60	8.38	90	0	NaHSO ₃
2,4,4-trime- thyl pentene- 2.....	760	7.8	6.4	3.6	13 ^b	(NH ₄) ₂ SO ₃
2,4,4-trimethyl pentene-2....	h	4.7	5.59	32	0	NaHSO ₃
Isoprene.....	760	7.8	9.0	21	0 ^j	(NH ₄) ₂ SO ₃
Isoprene.....	k	4.86	5.50	50	0 ^j	NaHSO ₃
α-Pinene.....	760	6.35	1.49	8	m	NaHSO ₃ - Na ₂ SO ₃
α-Pinene.....	n	5.5	6.48	18	m	NaHSO ₃

^aThe data herein tabulated have been selected from a group of some 200 experiments to illustrate the effect of several variables and the maximum yields observed.

^bBy bromide-bromate assay, hence less reliable than the corresponding values obtained by the permanganate method.

^c0.1 moles of NaNO_2 per mole of NaHSO_3 , introduced at one time.

^dAir not expelled from flask.

^eOxygen absent; 0.06 moles of NaNO_2 per mole of NaHSO_3 added over a period of 9 hours.

^fOxygen absent; 0.05 moles of NaNO_2 per mole of NaHSO_3 added over a period of 6 hours.

^gOxygen absent; 0.005 moles of NaNO_2 per mole of NaHSO_3 added over a period of 4.5 hours.

^hOxygen absent; 0.15 moles of NaNO_2 per mole of NaHSO_3 added over a period of 3 days.

^jProduct contains one double bond per molecule.

^kOxygen absent; 0.13 moles of NaNO_2 per mole of NaHSO_3 added over a period of 2 days.

^mMaterial entirely destroyed by permanganate.

ⁿOxygen absent; 0.25 moles of NaNO_2 per mole of NaHSO_3 added over a period of 2 days.

reaction at 300 volume per cent on the olefin taken. Both types of diluent, however, completely inhibited addition to less active bonds.

Wide latitude in ability to react with bisulfite is to be found among unsaturates, as measured by the maximum yield of sulfonate obtainable from each. This is practically quantitative from trimethylethylene, cyclohexene, and pentene-2, and ranges downward to from 3 to 25% for isoprene, α -pinene, and 2,4,4-trimethylpentene-2.

It has been established that for any given olefin under any given set of conditions there exists a sulfite-bisulfite buffer whose pH will not appreciably vary throughout the addition reaction. The ratio of sulfite to bisulfite in such a solution can be shown to be the same as the ratio of sulfate to sulfonate in the products: in other words, the sulfite content is oxidized and the bisulfite content adds, neither process causing serious change in pH. At this balance point the reaction attains its maximum rate and yield, hence such a buffer is referred to as that of "optimum pH" for the conditions employed. Since oxidation of bisulfite results in a great increase in the number of hydrogen

ions, a buffer originally containing an excess of this component will exhibit steadily decreasing pH during reaction. On the other hand, addition of sulfite to a double bond causes an increase in pH through liberation of hydroxyl ions; thus a buffer too alkaline to start with becomes even more basic by reaction. The actual value of the "optimum pH" is closely connected with the yield (for a constant cationic species). Both quantities have been found to vary not only with different olefins but also with the concentration of oxidant for any given olefin. Buffer considerations do not apply to nitrite reactions, as in these bisulfite is used alone and small differences in pH are unimportant. The reaction is still completely halted, of course, in solutions extremely acidic or basic.

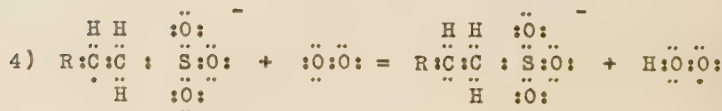
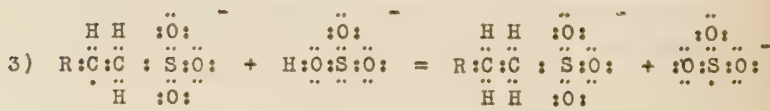
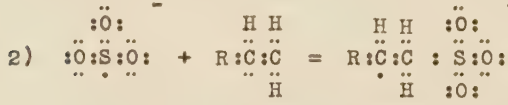
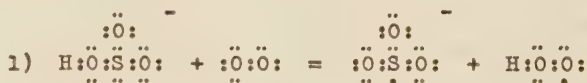
Ethylene diamine in any amount from 1/10 to 10 mole per cent was found to improve the low yields resulting from unreactive olefins at high oxygen concentrations, probably by suppression of the chain-breaking reaction. It was without effect on nitrite catalysis or where high yields were obtainable in its absence.

The production of isomeric sulfonates from trimethylethylene and pentene-2 is of interest not only as the first instance of its kind. Apparently the influence directing a bisulfite free radical to the more electronegative of two doubly-bonded carbon atoms possesses a quantitative relationship to the difference in their charges. From the data obtained from styrene and other terminal double bonds, where the magnitude of the discrepancy in electronegativity is comparatively great and but one product (considering the addition reaction alone) results, it might be concluded that the entering sulfonic acid group invariably becomes attached to the more electronegative carbon atom. The observations here reported serve to prevent such a misapprehension by demonstrating that much smaller differences of potential, such as that between methyl and ethyl groups, for example, in pentene-2, are not sufficient to direct the free radical to either carbon atom exclusively.

MECHANISM

The primary step in all bisulfite interactions is regarded as a collision between oxidant and bisulfite ion, resulting in the transfer of a hydrogen atom from the latter to the former and the generation of a free radical represented by the product in equation (1). This particle is absorbed by an olefin molecule to produce an intermediate organo-sulfonic acid free radical which by further collision is transformed into either saturated or unsaturated sulfonic acid. The saturated product results from acquisition of a hydrogen atom from a fresh bisulfite ion; a new bisulfite free radical is thereby generated and consequently the reaction involved is of a chain type. The unsaturated, or substitution, product is formed by collision of the intermediate with more oxidant, to which it loses a hydrogen atom. This process has no chain characteristics, since it consumes stoichiometric quantities of oxidizing agents. In nearly every case it is slow in comparison with the alternative route; hence the products of the average olefin-bisulfite reaction are poor in unsaturates.

The four steps are schematically summarized in the following equations:



The chain of the addition reaction is broken by impact of the bisulfite free radicals with more oxidant rather than with olefin:



Nitrite ions may replace oxygen in all except equation (4).

EXPERIMENTAL

Baker's monohydrated ammonium sulfite of 71% purity and General Chemical ammonium bisulfite solution, 25% sulfur dioxide, were employed, together with Merck's Reagent sodium bisulfite and Mallinkrodt Analytical grade sodium sulfite, anhydrous, assaying 79% sodium bisulfite and 86% sodium sulfite respectively. Ethylene diamine used was of the Eastman Technical grade.

Aqueous buffer solutions of highly reproducible pH for oxygen-promoted runs were prepared by mixing weighed quantities of sulfite and bisulfite, or of solutions of bisulfite and free base, and diluting until molar in total sulfurous acid salts. Reaction was carried out on a high-speed shaker in ordinary round-bottomed flasks with wired-in rubber stoppers, pierced by inlet tubes leading to a graduated reservoir of pure oxygen collected over water. The oxygen tension in the atmosphere over the reaction mixture in the vessel was fixed by using the undiluted gas, air, or a mixture of air with four volumes of nitrogen. In any case the concentration of the promoter was automatically kept constant by replacement with pure oxygen from the reservoir as fast as consumed. Overall pressure was maintained at atmospheric within narrow limits by never permitting the water level to rise far within the cylinder. Back diffusion was negligible because of the steady flow of oxygen into the flask. Oxygen runs were continued until iodine titration of an aliquot showed that only a negligible quantity of bisulfite remained, or until extreme pH changes greatly reduced the rate of reaction.

In carrying out such a reaction, the desired quantity of buffer was measured into a flask whose volume was two to three times that of the aqueous solution and about 1.5 moles of olefin per mole of total sulfurous acid salts were added. The appropriate atmosphere was then introduced, the stopper wired in and its inlet tube connected to the gas reservoir by a rubber hose. The contents of the flask were converted to an emulsion soon after the shaker was started. An experiment was considered

complete when the rate of reaction as measured by the rate of absorbtion of oxygen from the reservoir had dropped to a negligible level.

Solutions of bisulfite alone were used in nitrite-catalyzed additions. The sole change necessary in the apparatus was substitution for the gas inlet tube of two stopcocks. Air was displaced from the flask and liquid by passing in carbon dioxide rapidly for 15-20 minutes before shaking was commenced and excluded thereafter with fair efficiency by introducing the oxidant through the stopcocks. The catalyst was added as a 2.5 to 5 M. solution at the rate of 10 millimoles per mole of bisulfite every half-hour. Samples for assay of unreacted bisulfite were withdrawn in a capillary pipette from time to time through the stopcock bore without permitting ingress of appreciable oxygen. This type of run was stopped when the bisulfite concentration had fallen to such a point (0.15 M.) that fresh portions of oxidant caused a much smaller drop in the reducing power of the solution than at the start of the experiment.

Cyclohexene was obtained by dehydration of cyclohexanol with oxalic acid. Trimethylethylene was prepared by dehydrating tertiary amyl alcohol with concentrated sulfuric acid and distilling the product through an efficient column to separate the isomers. The fraction of b.p. 37-39°C. was collected for use. Pentene-2 resulted from identical treatment of diethyl carbinol, the fraction collected boiling between 35 and 38°C. The material referred to as α -pinene constituted the 152-156°C. cut from the fractionation of turpentine. Isoprene and 2,4,4-trimethylpentene-2 were prepared elsewhere and were used directly without further purification.

Completed reaction mixtures were separated from excess olefin and the aqueous portion clarified by an ether extraction or by filtering through a little carbon black. After potentiometric determination of pH and iodine titration of an aliquot to measure the unused bisulfite, the salt solution was evaporated to dryness in an open dish on the steam bath: directly if the reaction included the use of sodium or potassium bisulfite and oxygen. If nitrogen in any form was present, whether as ammonium bisulfite or as nitrite catalyst, 1.1 moles of sodium carbonate were added per mole of nitrogen before evaporation. In all such cases the dry residue from this treatment was further heated until

the escape of ammoniacal vapors could no longer be detected.

The resulting cake of mixed salts was finely ground and exhaustively extracted with boiling 80% alcohol. Evaporation of the solvent from the resulting clear solutions left behind a crystalline mass of organic sulfonate free from inorganic salts, which could then be further purified by recrystallization from alcohol of the appropriate strength.

The barium salts, which are sufficiently less soluble than the sodium to permit recrystallization from water, were obtained in two ways, by metathesis between the corresponding sodium salt and barium bromide in water and by treatment of the ammonium salts with excess barium hydroxide. In the latter instance the process was carried out on the crude solution produced by adding ammonium bisulfite to an olefin. After adding the base all the ammonia was removed by boiling and the sludge filtered. Saturation of the filtrate with carbon dioxide threw down excess barium hydroxide as the carbonate, leaving only organo barium sulfonate in the clear solution, from which it crystallized on concentration.

The proportion of unsaturated sulfonate in the total crude product was originally determined by means of standard bromate-bromide solution, but this procedure was later abandoned after it had been found to be much less reliable than the permanganate assay. The latter consisted of treating a weighed sample with cold neutral standard permanganate in excess, removing the precipitated manganese dioxide on asbestos, and back-titrating the excess oxidant with standard thiosulfate after addition of acid and potassium iodide. Since no stoichiometric equation for the oxidation of a double bond is followed exactly in this reaction, an empirical correction factor must be determined by assay of a sample of known composition if results of high accuracy are desired. This is not of great importance, however, where the unsaturation runs as low as in the samples herein reported.

The sulfonate resulting from addition of bisulfite to cyclohexene was analyzed as the potassium salt, after removal of all impurities oxidizable by permanganate.

Anal: Calc. for $C_6H_{11}SO_3K \cdot H_2O$	C=32.69%, H=5.95%, K=17.75%
Found	C=32.62%, H=5.77%, K=17.59%

The anhydrous salt was found to be very hygroscopic.

A portion of this material was converted into its amid

in the manner described by Kharasch, May, and Mayo³ A melting point of 93-94°C. was observed for both the product and its mixtures with an authentic specimen.

Anal.: Calc. for $C_6H_{13}SO_2N$ N=8.59% Found N=8.66%

Both isoprene and α -pinene yielded only deliquescent taffies which, because of lack of material and complete inability to crystallize either the barium or sodium salts, were not investigated beyond noting that the former still contained one double bond per molecule and that the latter was very thermolabile, even in solution, decomposing to a black tar on attempted recrystallization.

The sulfonates resulting from addition of bisulfite to pentene-2, trimethylethylene, and 2,4,4-trimethylpentene-2 were recrystallizable from water as barium salts and from alcohol as sodium or potassium salts. The phenylhydrazinium salts of the former two exhibited low melting points extending over a range of about 50°C., indicating the presence of appreciable quantities of isomers in each case. That of the latter carbonized without melting at about 250°C.

Attempts to prepare n-pentane 2- and 3-sulfonic acids, as well as isoamyl secondary sulfonic acid and tertiary amyl sulfonic acid from the respective bromides by several methods were all unsuccessful. No organic salt could be obtained; apparently HBr was split out in each case and the resulting olefins lost by volatilization.

³Loc. cit.

SUMMARY

1. The effect of oxidant concentration, solvents, and pH upon the oxygen- and nitrite-catalyzed addition and substitution of bisulfite in pentene-2, cyclohexene, isoprene, α -pinene, trimethylethylene, and 2,4,4-trimethylpentene-2 has been studied.

2. It is shown that the chief factors affecting the addition reaction of any olefin are pH and oxidant concentration, and that those affecting the corresponding substitution reaction are the kind of oxidant employed and its concentration.

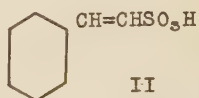
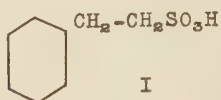
3. The addition product of bisulfite and olefins unsymmetrical about an internal double bond has been concluded to consist of a mixture of isomeric sulfonic acids.

PART II

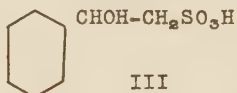
THE ADDITION OF BISULFITE TO STYRENE

DISCUSSION

Kharasch, May, and Mayo⁴ have reported that the products of the styrene-bisulfite reaction are 2-phenylethane sulfonic acid (I), in small amount, 2-phenylethylene sulfonic acid (II) as the main component, and a trace of benzoic acid.



The formation of all of these substances has been confirmed, but the material isolated in greatest amount (about 65% of the total yield in most cases) was 2-hydroxy-2-phenylethane sulfonic acid (III). This substance, on treatment with phosphorus pentachloride



and then with ammonia, loses the elements of water to form the same amid as II, and can be identified in a mixture of the two only by fractional crystallization of the sodium or potassium salt from dilute alcohol. It is not surprising, then, that the previous workers in the field did not suspect its presence, since for the most part they converted the crude salts directly into amids without previous purification. The few attempts that were made to work up the products by crystallization from water as the barium salts met with no success, since striking solubility differences between the various components do not exist under such circumstances.

The extent to which styrene will react with bisulfite, and hence the efficiency of the process, has been found to depend

⁴Loc. cit.

somewhat on the pH of the original aqueous salt solution, provided no further additions of material capable of altering the hydrogen ion concentration are made during the course of the reaction. The addition occurs, furthermore, under more extreme conditions of acidity and alkalinity than was formerly believed; such variations, however, are ineffective in causing appreciable changes in the ratio of products formed.

A small but reproducible variation in the proportion of the final products has been observed between two main classes of bisulfites: salts of the ammonium group, including all the alkylamines tested, give rise to somewhat greater amounts of the substitution product (II) at the expense of the addition product (I) than do those of the alkali metals. A number of examples of each type are given in Table 2. The anomalous behaviour of dimethylanilinium sulfite is probably attributable to the effect of the strongly electronegative phenyl radical, but confirmation of this hypothesis was hindered by the inability of diphenyl amines, because of their greatly lowered base strength, to form sulfites at all. Much the same sort of difficulty was encountered in an attempt to relate the variations between ammonium and alkali metal salts to base strength--here the bases of intermediate ionization constants, such as the alkaline earths, form water-insoluble sulfites. Dimethyl aniline possesses the additional peculiarity of furnishing unusually high yields, apparently as a result of its properties as a mutual solvent, together with its ability, when present in excess, to keep the solution at all times very close to neutrality. The behaviour of pyridine, which has similar characteristics, was found to be practically identical.

The rate of reaction was found to be effectively independent of the salt employed, but to be closely related to the oxygen concentration. Only the roughest of quantitative observations were made, but even these sufficed to indicate that the speed at which oxygen is consumed increases with its partial pressure. Conversely, the overall yield of organic sulfonates shows an inverse relationship to the oxygen tension. Increasing oxygen pressure furthermore results in favoring the substitution reaction (where it occurs to any appreciable extent, as with the ammonium group of salts already referred to) at the expense of the addition reaction. The small amounts of substitution encountered in the use of alkali metal bisulfites are independent

TABLE 2

THE ADDITION OF BISULFITE TO STYRENE^a

Cation of Bisulfite Used	Oxygen Tension, mm of Hg	pH		Total Per Cent Yield on Sulfites Reacted	Per Cent of Total Yield Present as: ^b		
		Initial	Final		I ^c	II ^d	III ^e
Sodium....	760	6.23	2.47	25	28	12	60
Sodium....	152	6.23	8.92	43	20	12	68
Sodium....	30	6.23	9.81	58	29	11	60
Ammonium..	760	6.52	6.90	30	8	28	64
Ammonium..	152	6.52	7.40	40	16	14	70
Ammonium..	30	6.52	8.72	68	20	7	73
Methyl-ammonium..	152	6.55	6.50	32	17	28	55
Dimethyl-ammonium..	760	5.97	2.00	29	21	17	62
Trimethyl-ammonium..	760	6.40	3.13	30	12	18	70
Ethylene-diammonium	152	7.02	7.95	33	8	10	82
Dimethyl-anilinium.	760	f	f	54	16	5	79
Pyridinium	760	g	g	66	23	20	57
Ammonium..	h	4.87	7.72	20	20	0	80
Ammonium..	j	7.81	1.43	15	50	0	50
Sodium....	k	4.74	7.11	25	35	0	65

^aThe results herein tabulated are representative examples of a group of 60 consistent experiments.

^bThe Roman numerals refer to the illustrative structural formulae on p. 16.

^cCalculated by difference.

^dBy permanganate assay.

^eWeighed as such.

^fpH not measured; maintained approximately constant near neutrality by excess dimethylaniline in second phase.

^gpH not measured; maintained approximately constant near neutrality by excess pyridine employed as solvent.

^hOxygen excluded; catalyzed by 0.3 moles of ammonium nitrite per mole of bisulfite reacted, added over a period of 12 1/2 hours.

^jOxygen excluded; catalyzed by 0.68 moles of ammonium persulfate per mole of sulfite reacted, added over a period of 3 1/2 hours.

^kOxygen excluded; catalyzed by 0.3 moles of sodium nitrite per mole of bisulfite reacted, added over a period of 6 1/2 hours.

of oxygen concentration, as is the ratio of hydroxy sulfonate (III) to the other products in all oxygen-promoted experiments. The yield of the latter, in fact, remained substantially constant regardless of any alteration of experimental conditions.

The possible effect of salt concentration was investigated in one experiment conducted according to the method of Kolker and Lapworth,⁵ as amended by Ashworth and Burkhardt⁶ to include styrene. The use of M/6 bisulfite solution in place of the usual M/1, in a procedure precluding rate comparisons, gave the same products in about the customary yield.

Replacement of oxygen by nitrite or perdisulfate ion as reaction promoter results in complete suppression of the substitution reaction, the proportions of both the addition product and the hydroxy sulfonate being compensatingly increased. Overall yields are here to some extent influenced by the rate at which the oxidant is introduced, but even when the latter is added at the minimum convenient speed they are no better than those resulting from use of oxygen at one atmosphere pressure.

Nitrate ion has been found to be of very slight value as an oxidant in bisulfite additions in comparison with the three foregoing materials. The observable effect, in fact, may readily be ascribed not to the nitrate itself but to the few per cent of nitrite generally present as impurity in nitrates.

Since it was not found possible to convert any of the three major products into any other by any means comparable to conditions existing during the reaction or the subsequent isolation of the resulting sulfonates, it was concluded that each is a primary reaction product. For instance, a pure sample of each of the three compounds in turn was treated first with hot acid, then with hot alkali, and finally with sodium bisulfite and oxygen. With one exception the starting materials were in every case recovered unchanged, and in that single instance not one of the previously known substances but a new compound was obtained. Specifically, the action of bisulfite and oxygen upon the

⁵Kolker and Lapworth, J. Chem. Soc., 127, 307 (1925).

⁶Ashworth and Burkhardt, ibid., 130, 1791 (1928).

substitution product results in the addition of another molecule of bisulfite to the double bond with the production in good yields of 2-phenylethane-1, 1-disulfonic acid (IV). From the fact that this compound is never formed during treatment of styrene with bisulfite, even in those experiments in which subsequent analysis shows the unsaturated acid to have been present in the greatest quantities ever observed, it is evident that its formation is prevented by the presence of excess styrene.

It was anticipated after discovery of the hydroxy sulfonate that benzoylmethane sulfonic acid (V) might also logically be included among the products of the reaction, as a result of further oxidation of the former substance. No trace of it, however, has thus far been isolated from this source. It has furthermore been



observed in this connection that the hydroxy compound, in view of its structure as a water-soluble secondary alcohol, is surprisingly resistant to oxidation. It is stable to both acid and alkaline permanganate in the cold, and even at 90-100° the oxidation is relatively slow.

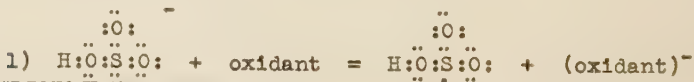
This observation was made the basis of an attempt to determine yields of unsaturated sulfonate without separation of the crude mixtures into their components. Accurately weighed samples were treated with cold neutral permanganate in excess, the solution freed from precipitated manganese dioxide, and added to excess acid potassium iodide solution. By titrating the liberated iodine with thiosulfate a measure of the unreacted permanganate was obtained. Under such conditions the substitution product is quickly and completely oxidized. The reaction, however, does not follow a predictable stoichiometric course, and as a result it is necessary to standardize the permanganate against a sample of unsaturated sulfonate or sulfonamid of known purity rather than against any of the usual inorganic standards. As a further qualification, it was found that while pure hydroxy sulfonate is not attacked by the oxidizing agents employed, it does react to a varying extent when present in a mixture of

products containing the unsaturated derivative and thus leads to extremely inconsistent results. Its removal is very conveniently effected, fortunately, leaving only addition and substitution products in the remainder. These are nearly impossible to separate, but since the former, unlike the hydroxy compound, is uniformly inert, assay of the latter with permanganate standardized as described gives highly reproducible results.

MECHANISM

The data herein presented are entirely in accord with the thesis of Kharasch, May, and Mayo⁷ that the reaction proceeds through a free-radical intermediate. The evidence for this hypothesis lies in the facts that reagents capable of oxidizing bisulfite are necessary for any interaction to occur and that the products (aside from the benzoic acid arising probably from the direct oxidation of styrene) are exclusively those accountable for by "abnormal" addition to the double bond. The observations here presented furthermore provide a more quantitative basis for the conclusion that the favored reactions between bisulfite and styrene are unlike those which occur with other olefins in that chains are apparently not important in this particular case. It is true that a chain reaction best accounts for the simple addition product (I), but this class of compound, which constitutes the main product of most unsaturated hydrocarbons, is formed to only a very limited extent from styrene. Reference to the footnotes to Table 2 will show the comparatively large amounts of oxidant consumed in the addition of bisulfite to the latter olefin, indicating a stoichiometric rather than a chain reaction. In addition, the proportion of sulfite lost as sulfate is not compatible with a self-propagating reaction.

The first steps, wherein a bisulfite free radical, produced by the oxidant⁸ capturing an electron from a bisulfite ion, is absorbed by a styrene molecule, have already been thoroughly discussed in Part I, and are reproduced below as equations (1) and (2) only for the sake of convenience.



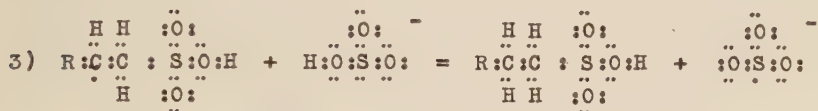
⁷Loc. cit.

⁸The term "oxidant" as used in this dissertation refers to any molecule, atom or free radical capable of accepting an electron or a hydrogen atom from either bisulfite ion, bisulfite free radical, or the organic free-radical complex.

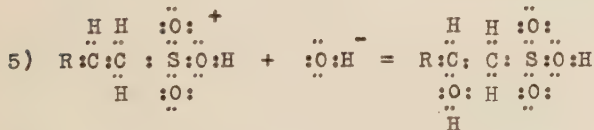
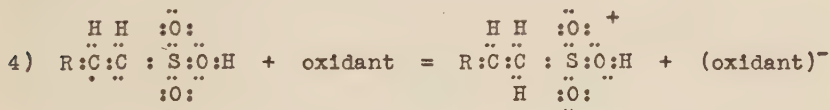


The resulting free-radical complex is then subject to three types of further change, each giving rise to a different product:

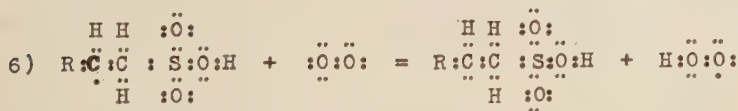
a. The simplest case is that in which a hydrogen atom is acquired by collision with another bisulfite ion, as in equation (3), with the formation of 2-phenylethane sulfonic acid and regeneration of sulfite-ion free radical.



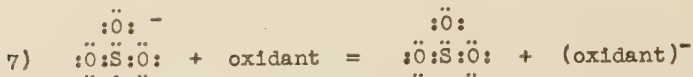
b. The intermediate may collide with the oxidant and in doing so lose to the latter its unpaired electron. The positively charged molecule thus created readily combines with a negative ion from the solution to form 2-hydroxy-2-phenylethane sulfonic acid.



c. The third type of impact, that which is responsible for the substitution reaction and the formation of 2-phenethylene sulfonic acid, occurs only in the presence of oxygen. For this reason the nature of the oxidant in equation (6) is specified.



Finally, bisulfite free radicals are transformed to sulfate by a second collision with oxidant, before they can effect combination with styrene, as in equation (7).



The loss of two electrons to the oxidant has been written, in those reactions where it takes place (equations 4 and 6), in two steps for several reasons. In the first place the removal of both charges at once from sulfite ion results in molecular sulfur trioxide, which in aqueous solution would at once stabilize itself as totally unreactive sulfate ion. Furthermore, if it were possible for sulfur trioxide to exist in dilute solution long enough for it to share the free electron pair of styrene, the resulting formation of hydroxy sulfonates would be a general property of the bisulfite addition instead of being peculiar to styrene, as observed. Lastly, the method employed permits each equation to follow in sequence from a common foundation, whereas the introduction of a two-electron transfer would require the postulation of two separate species of inorganic free radicals.

It is significant that the apparent relative stabilities of the substituted ethylenesulfonate free radicals fall in the same order as those of the corresponding substituted methyl free radicals. The latter, arranged according to increasing ability to independent existence, are methyl, phenylmethyl, diphenyl methyl, and triphenylmethyl. Of the former, the alkylethane sulfonate free radicals are relatively short-lived and are the most reactive, with the result that practically every collision with bisulfite is effective, and the products are mainly simple addition compounds. Arylethane sulfonate free radicals, on the other hand, are probably of much greater stability. Reaction of these with bisulfite may be assumed to require an appreciable activation energy. Consequently, fruitful impacts are largely with the oxidant and lead to substitution or the introduction of hydroxyl groups in a large proportion of the intermediate complexes. The observed phenomena thus follow predictions based on consideration of the probable electron patterns as defined by the theory of electronegativity.⁹

⁹Kharasch and Reinmuth, J. Chem. Education, 8, 1703 (1931); Kharasch and Flenner, J. Am. Chem. Soc., 54, 674 (1932).

EXPERIMENTAL

A detailed description of the inorganic reagents used, the apparatus, and the manner of conducting the experiments may be found in Part I under this same heading.

Styrene, obtained through courtesy of the Bakelite Corporation, was used both as received (containing small amounts of hydroquinone) and freshly distilled in vacuo. No difference between the two kinds was perceptible in any bisulfite addition. Ethylenediamine sulfite was prepared by diluting the Eastman Technical base (60% $(\text{CH}_2\text{NH}_2)_2$ in water) with two volumes of alcohol and saturating with sulfur dioxide. The granular white precipitate, after collection on a filter, an alcohol and ether wash, and air-drying, melted at 176°C . Iodine titration of a sample for sulfur dioxide showed the material to be 99% pure $(\text{CH}_2\text{NH}_2)_2\text{SO}_3$. The yield was nearly quantitative. Concentrated stock solutions of substituted ammonium bisulfites were made up by absorbing the maximum of sulfur dioxide in 25-35% solutions of base in water as supplied by Commercial Solvents Corporation. Pyridine was diluted with one-fourth its weight of water and sulfur dioxide introduced until its concentration was approximately molar. This reagent was used without further dilution. Dimethyl aniline was suspended in water and treated with sulfur dioxide until the mixture became homogeneous. More water was added to the resulting solution to reduce its sulfite content to molar before use.

Sulfite alone was used in reactions catalyzed by persulfate.

The proportion of styrene present was in all instances the same: mole for mole with the total sulfurous salts. Since even at best a large part of the latter are oxidized to sulfate, the styrene was always actually in excess.

Among the solvents tested, two, 95% alcohol and liquid ammonia, failed to produce any evidence of reaction whatever. Dimethylaniline was the base present in the former trial, and in the latter the solvent itself functioned as proton acceptor. This second run was made by bubbling air through the solution under stirring in place of the usual technique of shaking in a closed system. The action of nitrite on either of these mixtures

was not investigated. Water proved to be a generally reliable medium. The most desirable results were obtained in 80% aqueous pyridine, in which a much more nearly homogeneous solution is attainable than in water. Even under high oxygen pressures the ratio of sulfonate to sulfate formed in such a run is unusually favorable.

In the treatment of completed reaction mixtures (see Part I) small variations on the regular procedure were desirable in several special cases: for instance, pyridine was not evaporated off freely but was recovered by distilling from the salts in vacuo, after addition of water to cause separation of excess styrene and of sodium carbonate to set the pyridine free from its salt combinations. Dimethylaniline was mechanically separable from the alkalized solution.

Separation of organic from inorganic salts was carried out as before. The organic residue from evaporation of the alcoholic filtrate was then further treated by boiling with 10 cc. of 90% alcohol per gram, cooling to room temperature and filtering. The insoluble material from this step consists of nearly pure hydroxyphenethyl sodium sulfonate, which may efficiently be recrystallized from 70% alcohol as pearly white platelets. From the filtrate above may be obtained, by evaporation to dryness, a mixture of phenethyl and phenethylene sodium sulfonates. These may be recrystallized from 85-90% alcohol or from saturated aqueous salt solutions, but the former solvent often leads to difficulty filterable pastes and the latter to products contaminated by inorganic salts. A much more satisfactory procedure is to convert them to barium salts as previously described and recrystallize from water. The sodium salts of both these compounds are obtained as small, shiny, white plates from alcohol or as coarse, thin, transparent plates from brine. The barium salts crystallize from water as tiny white scales, containing one molecule of water of crystallization. Either of the above materials may be obtained in a pure state by either method from a mixture with the other in which it predominates. The saturated sulfonate may also be freed from any proportion of the unsaturated by destroying the latter with potassium permanganate. No scheme has yet been devised for the separation of both components of an approximately equimolar mixture, or for isolation of small amounts of unsaturated sulfonate from a mixture rich in the saturated.

Both the saturated and unsaturated sulfonates were converted to amids by the action of phosphorus pentachloride followed by ammonia. That obtained from the former melted at 124°C . and that from the latter at 143°C ., as reported by the previous workers.¹⁰ In neither case did a mixed melting point with an authentic specimen show any depression.

Sodium 2-phenylethane sulfonate: $\text{C}_8\text{H}_9\text{SO}_3\text{Na}$

Anal.: Calc. C = 46.15%, H = 4.36%, Na = 11.05%

Found C = 45.80%, H = 4.26%, Na = 11.01%

Barium 2-phenylethylene sulfonate monohydrate: $(\text{C}_8\text{H}_7\text{SO}_3)_2\text{Ba}$, H_2O

Anal.: Calc. C = 36.83%, H = 3.09%, Ba = 26.32%

Found C = 37.00%, H = 3.27%, Ba = 26.64%

Sodium 2-hydroxy-2-phenylethane sulfonate: $\text{C}_8\text{H}_9\text{SO}_4\text{Na}$

Anal.: Calc. C = 42.85%, H = 4.05%, Na = 10.26%

Found C = 42.69%, H = 4.05%, Na = 10.24%

Establishment of structure of sodium 2-hydroxy-2-phenylethane sulfonate. The analytical data reproduced above for this salt correspond to those calculated for sodium 2-phenylethylene sulfonate containing one molecule of water per mole. Such a hydrate has never been prepared, however (it is only the barium salt which forms a stable hydrate). Furthermore, a sample of the material was observed to have lost no weight whatsoever after standing for a week over phosphorus pentoxide in vacuo. The stability of the compound to permanganate, moreover, shows it to be saturated, and the fact that when it is oxidized under vigorous conditions only benzoic acid (identified by its mixed melting point of 123°C . with a known sample) can be isolated in high yield, indicates that all substituents are in the side chain. Treatment with phosphorus pentachloride in the cold results in a vigorous exothermic reaction, accompanied by the evolution of much hydrogen chloride and yielding a sulfonyl chloride which was transformed by the action of ammonia into the unsaturated amid of melting point 143°C . The overall conversion of the salt into amid is about 70%. This reaction, together with the stability of the salt to both acid and base (no inorganic sulfur is liberated even on long boiling), proves the absence of sulfate ester and the position of

¹⁰Kharasch, May, and Mayo, loc. cit.

the sulfonic group as β to the phenyl; the former because sulfate esters not only are easily hydrolyzed to alcohols and sulfuric acid but can not yield sulfonyl chlorides on treatment with PCl_5 , the latter because α -phenyl sulfonic acid groups are known to be split off by PCl_5 treatment and not to rearrange to furnish β -sulfonyl chlorides. The hydroxyl can not also be β to the phenyl, as compounds having a hydroxyl on the same carbon atom as a sulfonic acid group are known to be easily decomposed by either acid or base into sulfur dioxide (or one of its salts) and the corresponding carbonyl compounds. The configuration thus arrived at has been shown to be correct by synthesis from styrene bromhydrin (vide infra).

The hydroxyl group here present exhibits none of the reactions characteristic of its class. All attempts to esterify it uniformly failed. No treatment with reagents designed to replace it with halogen was successful: either the salt was recovered unchanged or only the unsaturated derivative was obtained.

Styrene bromhydrin was prepared according to Read and Reid,¹¹ although it was not found possible to reproduce the high (95-98%) yields reported. Under the best circumstances only 80 to 85% of the bromine employed added as hypobromous acid, the remainder forming styrene dibromide, while as little as 60% of the theoretical quantity of bromhydrin was isolated from larger runs. The two products were efficiently separated by thoroughly cooling the crude oil in the icebox and filtering the still-liquid bromhydrin from the crystallized dibromide.

Styrene iodohydrin was prepared by the method of Brunel.¹²

Styrene dibromide was obtained both as a byproduct in the manufacture of the bromhydrin and in the manner of Evans and Morgan.¹³

Sodium 2-hydroxy-2-phenylethane sulfonate resulted from treatment of styrene brom- or iodohydrin with aqueous sodium sulfite according to the procedure of Houlton and Tartar¹⁴ for

¹¹Read and Reid, J. Chem. Soc., 130, 1487 (1928).

¹²Brunel, Ann. Chem (vii), 6, 219 (1905).

¹³Evans and Morgan, J. Am. Chem. Soc., 35, 56 (1913).

¹⁴Houlton and Tartar, ibid., 60, 544 (1938).

alkyl halides in general. It was found to be identical in all its properties, physical and chemical, with that fraction of the reaction products analytically identified as such.

Phenylhydrazinium 2-hydroxy-2-phenylethane sulfonate was prepared by the method of Latimer and Bost¹⁵ for phenylhydrazinium salts, from samples of hydroxy sulfonate resulting from both addition to styrene and metathesis of the bromhydrin. It crystallized from alcohol as small yellowish plates, very soluble in water and melting sharply at 180-181°C. with decomposition. Mixtures from the several sources showed no depression of the melting point.

Sodium 2-phenylethylene sulfonate was produced in high yield from the hydroxy sulfonate by grinding with excess PCl_5 , throwing into water and refluxing the resulting water-insoluble sulfonyl chloride with excess saturated aqueous sodium carbonate solution to complete disappearance of the oily layer. On cooling the unsaturated salt separated as a loose mass of large, thin, transparent plates.

Sodium benzoylmethane sulfonate was also prepared according to Houlton and Tartar.¹⁶ It crystallized from 85% alcohol as soft, asbestos-like fibers. No amid could be obtained from this material, nor was any fraction even remotely resembling it in any of its properties ever isolated from the various reaction products.

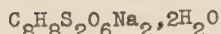
The addition of sodium bisulfite to the substitution product: Ten grams (0.05 moles) of sodium 2-phenylethylene sulfonate, from either direct substitution or the hydroxy sulfonate (*supra*), was dissolved in a solution of 10.5 grams (0.1 mole) of sodium bisulfite and 25 grams (0.2 mole) of sodium sulfite in 250 cc. of water and shaken with oxygen in the same apparatus used for styrene additions until absorbtion of the gas ceased. The solution was evaporated to dryness on the steam bath and the residue finely ground. It was then exhaustively extracted with boiling 70% alcohol and the soluble salts isolated by evaporation of the filtrates. The products separated from smaller volumes of dilute alcohol as a pulpy mass of soft, silky needles grouped in rosettes. This material no longer gave a positive permanganate

¹⁵Latimer and Bost, ibid., 59, 2500 (1937).

¹⁶Loc. cit.

test for unsaturation, but was still oxidizable by more powerful reagents to benzoic acid, showing that the additional molecule of bisulfite indicated by the analysis had added to the double bond to form a side-chain disulfonate. Treatment with PCl_5 eliminated a sulfonic acid group and caused extensive decomposition. The only amid isolable, and that in extremely small yield, proved to be the β -phenethylene sulfonamid of melting point 143°C .

Disodium 2-phenylethane-1, 1-disulfonate dihydrate:



Anal.: Calc. Na = 13.28%, H_2O = 9.54%

Found Na = 13.12%, H_2O = 9.22%

Disodium 2-phenylethane-1, 2-disulfonate was prepared from styrene dibromide by Houlton and Tartar's¹⁷ procedure. It crystallized from 70% alcohol as small, elongated prisms totally unlike the needles described immediately above. The action of PCl_5 and ammonia, however, on this disulfonate was practically identical with that on the other, only a very small quantity of the same unsaturated amid resulting.

Phenylhydrazinium 2-phenylethane-1, 2-disulfonate, synthesized according to the instructions of Latimer and Bost,¹⁸ melted sharply at $187\text{--}188^\circ\text{C}$. with decomposition. It crystallized from alcohol as microscopic yellowish scales, very soluble in water.

Phenylhydrazinium 2-phenylethane-1, 2-disulfonate was prepared in the same manner as the above from the addition disulfonate. This salt possesses a far lower water solubility than its isomer. It may be recrystallized from water as tiny yellowish scales, and melts at no definite temperature. In a slowly-heated bath it darkens at 173°C . and sinters at $180\text{--}185^\circ\text{C}$. with decomposition to brownish-black products which are thereafter infusible. When introduced into a pre-heated bath at $195\text{--}200^\circ\text{C}$. it visibly melts with evolution of gas and transformation into the same dark residue.

It was not found possible to prepare by unambiguous synthesis the β, β -disulfonate the addition material is believed to be. However, it has been shown (1) that both groups are in

¹⁷Loc. cit.

¹⁸Loc. cit.

the chain, (2) that one at least must be terminal, and (3) that the compound is not identical with the α, β -disulfonate of known structure. By elimination, then, the configuration must be that represented by formula IV (p. 20), 2-phenylethane-1, 1-disulfonic acid.

SUMMARY

1. The effect of oxidant concentration, solvents and pH upon the oxygen-, nitrite- and persulfate-catalyzed addition and substitution of bisulfite in styrene has been studied.

2. The interaction of styrene and bisulfite yields mainly 2-hydroxy-2-phenylethane sulfonic acid.

3. A mechanism involving oxygen has been proposed to explain the substitution of bisulfite in styrene, and one independent of the nature of the oxidant to account for the formation of the hydroxy derivative.

4. Four new sulfonic acids have been prepared, some of their properties studied, and the constants of some of their derivatives noted.

